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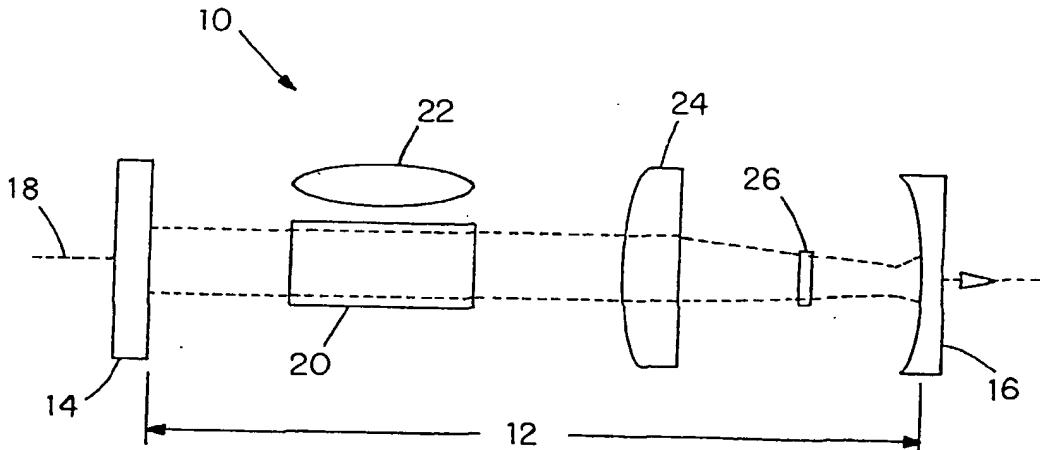
(57) Abstract: A saturable absorber Q-switch includes a monocrystalline lattice having the formula $Mg_{1-x}Co_xAl_yO_z$ where x is greater tha 0 and less than 1, y is greater than 2 and less than about 8, and z is between about 4 and 13. The lattice has tetrahedral and octehedral positions, and most of the magnesium and cobalt occupy tetrahedral positions. In one embodiment, the molar ratio of aluminium to the combined amount of magnesium and cobalt in the monocrystalline lattice can be controlled during growth of the monocrystalline lattice to thereby form a saturable absorber Q-switch that exhibits a $^4T_1$ spectrum for the cobalt ion of at least about 1544 μm. In another embodiment, a laser system, such as an Er:glass laser system, includes a saturable absorber-Q-switch that includes a monocrystalline lattice wherein the molar ratio of aluminium to the combined amounts of magnesium and cobalt exceeds 2:1, and preferably is about 6:1, and wherein essentially all of the magnesium and cobalt components of the monocrystalline occupy tetrahedral positions of the lattice.

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COBALT-DOPED SATURABLE ABSORBER
Q-SWITCHES AND LASER SYSTEMS

RELATED APPLICATION

This application claims priority under 35 U.S.C. § 119 or 365 to U.S.

5   Application No. 09/863,013, filed May 22, 2001, the entire teachings of which are

incorporated herein by reference.

BACKGROUND OF THE INVENTION

Q-switching is a method for obtaining single laser pulses of very high power

by protracting the period of population inversion of electrons in excited states just

10   prior to emission. Extending the period of population inversions typically can be

achieved acousto- or electro-optically by use of shutters, mechanically (with an

orthogonal mirror or rotating mirror), or by use of saturable absorbers (in the form of

dyes or doped crystals).

The term "Q-switching" is a reference to the fact that a "Q-factor" or

15   "Quality factor," which can be defined as $v/\Delta v_c$, where v is cavity resonance

frequency, and Δv_c is cavity linewidth, shifts from a very low value to a very high

value during laser pulse emission. More specifically, population inversion of

electrons is extended by blocking emission from the laser cavity. At the time a laser

pulse is to be emitted, the blockage is removed, thereby causing the threshold gain of

20   electrons to be deliberately and suddenly reduced. Population inversion is much

higher than the threshold gain value, and actual gain greatly exceeds cavity losses.

As a result, the excited states are quickly depopulated, causing energy to be

discharged in a single laser pulse. The sudden discharge causes actual gain to be

reduced to a point below the threshold value, thereby terminating the pulse.

25   Saturable absorber Q-switches operate passively, whereby absorptivity of the

laser wavelength decreases with increasing irradiance until "bleaching" occurs.

Population inversion increases until the Q-switch is bleached, at which time the

threshold value is reduced, resulting in a laser pulse. Passive Q-switches typically

are easy to implement relative to other mechanisms. Historically, examples of saturable absorber Q-switches are dyes, such as bis 4-dimethyl aminodithiobenzyl-nickel (BDN) dissolved in 1,2 dichloroethane for Nd:YAG lasers, and gases, such as SF_6 for CO_2 lasers.

5   More recently, solid state Q-switches have been employed that include crystals doped with tetrahedrally coordinated Co^{2+} ions as a tunable laser source in wavelengths that range from about 1.5 to about 2.3 µm. Among the crystals that have been doped with Co^{2+} ions for 1.34 µm Nd^{3+}:$YA1O_3$ and 1.54 µm-Er^{3+}: glass lasers are $Y_3Al_5O_{12}$,

10    $Y_3Sc_2Ga_3O_{12}$, $LaMgAl_{11}O_{19}$, $MgAl_2O_4$ (MALO) and ZnSe. $MgAl_2O_4$ crystals, otherwise known as spinel, include tetrahedral and octahedral positions. Co^{2+} dopant ions displace Mg^{2+} ions from tetrahedral positions of the crystal. The amount of Co^{2+} ion dopant in $MgAl_2O_4$ crystals typically ranges from about 0.0003 atomic weight percent to about 0.05 atomic weight percent. However, the frequency of the

15   peak emission of doped solid state passive Q-switches typically is not affected by the amount of dopant. Further, the efficiency of a Q-switch (and, thus, the power of the laser pulse) is significantly diminished if it does not have an absorption band that matches the lasing transition. For example, spinel having the empirical formula of $MgAl_2O_4$ and doped with Co^{2+} typically has an absorption band ($^4T_1$ spectrum) of

20   about 1536 nanometers (nm), whereas the lasing transition of Er:Yb:glass lasers is about 1540 nm. Generally, the efficiency of cobalt-doped spinel Q-switches in Er:Yb:glass and other lasers is limited by the difference in specific absorption bands from the lasing transition wavelengths of such lasers.

Therefore, a need exists to significantly diminish or eliminate the above-

25   mentioned problems of cobalt-doped saturable absorber Q-switches.

SUMMARY OF THE INVENTION

This invention is directed to a cobalt-doped saturable absorber Q-switch, to a laser system that employs a cobalt-doped saturable absorber Q-switch, and to a method of forming a cobalt-doped saturable absorber Q-switch.

In one embodiment, the saturable absorber Q-switch includes a monocrystalline lattice having the formula $Mg_{1-x}Co_xAl_yO_z$ where x is greater than 0 and less than 1, y is greater than 2 and less than about 8, and z is between about 4 and about 13. The lattice has tetrahedral and octahedral positions, and most of the

5   cobalt and magnesium occupies tetrahedral positions. In a preferred embodiment, essentially all of the cobalt and magnesium occupies tetrahedral positions of the monocrystalline lattice.

In a laser system of the invention, a laser resonator cavity has a resonant axis and a lasing element within the resonator cavity. Suitable means optically pump the

10   lasing element. A saturable absorber Q-switch lies along the resonant axis of the laser resonator cavity. The Q-switch includes a monocrystalline lattice having a formula

$Mg_{1-x}Co_xAl_yO_z$ where x is greater than 0 and less than about 1, y is greater than 2 and less than about 8, and z is between about 4 and about 13. The monocrystalline

15   lattice has tetrahedral and octahedral positions, and most of the magnesium and cobalt occupy tetrahedral positions. In a preferred embodiment, essentially all of the magnesium and cobalt occupy tetrahedral position of the monocrystalline lattice. In one embodiment, the lasing element is an Er:Yb:glass laser (or any laser source of 1.5-1.6 μ frequency). In another embodiment, the laser element is a $Nd^{3+}:YAlO_3$

20   lasing element.

A method of forming a monocrystalline lattice of a saturable absorber Q-switch of the invention includes forming a melt of magnesium, cobalt, aluminum and oxygen, wherein the molar ratio of magnesium:cobalt:aluminum is (1-x):x:y, where x is greater than 0 and less than about 1, and y is greater than 2 and less than

25   8. A spinel seed crystal is immersed in the melt and rotated at a rate in a range of between about 4 and about 12 revolutions per minute, while withdrawing the seed crystal from the melt at a rate in a range of between about 0.04"/hr and about 0.1"/hr to thereby form the monocrystalline lattice. In one embodiment, the melt is formed by combining MgO, Co_3O_4 and Al_2O_3 powders, and then heating the combined

30   powders to a temperature sufficient to form the melt.

The present invention has several advantages. For example, the saturable absorber Q-switch of the invention includes a ratio of aluminum to magnesium that is greater than that of spinel ($MgAl_2O_4$) having an equal amount of cobalt dopant. Despite the relatively high ratio of aluminum to magnesium, most or essentially all
5 magnesium and cobalt dopant occupy only tetrahedral positions of the crystal. Modification of the relative amount of aluminum to magnesium in the saturable absorber Q-switches of the invention enables adjustment of the $^4T_1$ spectrum of cobalt dopant to more closely match a peak of 1544 nanometers, which is the lasing -wavelength of erbium:ytterbium:glass (Er:Yb:glass) lasers. In another embodiment,
10 modification of the relative amount of aluminum to magnesium also enables emission of a band at about 1340 nanometers, which is about the lasing wavelength of Nd^{3+}:YAlO_3$ lasers. Both emission bands can significantly increase the efficiency of saturable absorber Q-switches employed with such lasers. Also, the saturable absorber Q-switches of the invention generally are relatively stable at reduced
15 temperatures, such as at about 8 Kelvin (K).

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of one embodiment of the laser system of the invention, employing a cobalt-doped Q-switch of the invention.

Figure 2 shows light absorption in a 1:3 spinel as a function of wavelength at
20 8 Kelvin (K).

Figure 3 shows light absorption in a 1:3 spinel as a function of wavelength at 300 Kelvin (K).

Figure 4 shows fluorescence intensity of a 1:3 spinel as a function of wavelength at 8 Kelvin (K).

25 Figure 5 shows fluorescence intensity of a 1:3 spinel as a function of wavelength at 300 Kelvin (K).

Figure 6 is an overlay of Figures 4 and 5, as a comparison.

DETAILED DESCRIPTION OF THE INVENTION

The features and other details of the invention will now be more particularly described with reference to the accompanying figures and pointed out in the claims. It will be understood that the particular embodiments of the invention are shown by
5   way of illustration and not as limitations of the invention. The principal features of this invention can be employed in various embodiments without departing from the scope of the invention.

In one embodiment, the invention is a laser system that employs a saturable absorber Q-switch having a monocrystalline lattice, wherein the monocrystalline
10   lattice has a formula of $Mg_{1-x}Co_xAl_yO_z$, and wherein x is greater than 0 and less than about 1, y is greater than 2 and less than about 8, and z is between about 4 and about 13. The monocrystalline lattice of the saturable absorber Q-switch employed in the laser system of the invention has tetrahedral and octahedral positions, and most of the magnesium and cobalt occupy tetrahedral positions. Preferably, essentially all of
15   the cobalt and magnesium occupy tetrahedral positions.

An example of a laser system of the invention is shown in Figure 1. As shown therein, laser system 10 includes resonator cavity 12. Resonator cavity 12 is defined by flat mirror 14 and outcoupler mirror 16. Flat mirror 14 and outcoupler mirror 16 are oriented along a resonant axis 18, whereby a light beam within
20   resonator cavity 12 can operate in a cavity mode. Lasing element 20 is located along resonant axis 18 within resonator cavity 12. Typically, lasing element 20 is a cylindrical rod oriented parallel to resonant axis 18. Examples of suitable lasing elements include Er:Yb:glass (erbium:ytterbium:glass), Er:glass (erbium doped into a phosphate glass host) and Nd^{3+}:$YAlO_3$ (erbium doped into a yttrium-aluminum
25   oxide host).

A suitable means for optically pumping the lasing element, optical pump 22, is proximate to lasing element. Focusing lens 24 is located between lasing element 20 and outcoupler mirror 16.

Q-switch 26 is located between focusing lens 24 and outcoupler mirror 16.
30   Saturable absorber Q-switches of the invention include a monocrystalline lattice of a cobalt-doped spinel-like material wherein the molar ratio of aluminum to the sum of

magnesium and cobalt components of the monocrystalline lattice exceeds 2:1. More specifically, the saturable absorber Q-switch of the invention includes a monocrystalline lattice having the formula $Mg_{1-x}Co_xAl_yO_z$ where x is greater than 0 and less than 1, y is greater than 2 and less than 8, and z is between about 4 and 13.

5   A "1:1 spinel" refers to an embodiment wherein y is about 2. A "1:2 spinel" refers to an embodiment where y is about 4. A "1:3 spinel" refers to an embodiment where y is about 6. Most of the magnesium and cobalt of the saturable absorber Q-switch occupy tetrahedral positions of the monocrystalline lattice. In a preferred embodiment, essentially all of the cobalt and magnesium occupy tetrahedral

10   positions.

In one embodiment of the invention, the monocrystalline lattice has a value of z of about 4. In another embodiment, y is about 4 and z is about 7. In still another embodiment, y is about 6 and z is about 10. Generally, the saturable absorber Q-switch has a $^4T_1$ spectrum between about 1537nm and about 1544nm. In

15   one preferred embodiment, wherein the lasing element of the laser system of the invention is an Er:Yb:glass lasing element, the value of y is sufficient to cause the monocrystalline lattice of the saturable absorber Q-switch to have a $^4T_1$ spectrum of cobalt ion (Co^{2+}) to emit light at a wavelength of at least about 1.54 μm (1540nm). In an especially preferred embodiment, the saturable absorber Q-switch has an

20   absorption band of about 1544nm.

In another preferred embodiment, such as wherein the lasing element is a Nd^{3+}:$YAlO_3$ lasing element, the value of y is sufficient to cause the monocrystalline lattice to have an absorption band of between about 1337nm and about 1365nm, such as an absorption band of 1337nm, 1360nm, 1365nm or, most preferably, about

25   1340nm.

In one embodiment, the excited state absorption for the cobalt ion in the saturable absorber Q-switch of the invention is about the same as that of a saturable Q-switch absorber wherein a molar ratio of aluminum to the combined magnesium and cobalt amount is about 2. Generally, the unit cell dimension of the

30   monocrystalline lattice will be less than about 8.085 Å. In a preferred embodiment, the unit cell dimension is between about 7.970Å and about 8.083Å. In still another

embodiment, the saturable absorber Q-switch of the invention has a decay time (τ_{31}) greater than about 30×10^{-6} seconds.

Typically, the amount of cobalt ion in the saturable absorber Q-switch of the invention is greater than about 0.02 atomic percent. Preferably, the amount of cobalt

5   ion present is in an amount in a range of between about 0.02 and about 0.043 (atomic?) weight percent of the monocrystalline lattice.

The saturable absorber Q-switches of the invention can be formed by use of a spinel seed ($MgAl_2O_4$) having a major axis oriented along the <111> axis. Preferably, the spinel seed is cylindrical. The crystal is grown, for example, in an

10   inductively-heated ten kHz radiofrequency (RF) generator. Control of crystal growth can be maintained by use of suitable computer software, such as Automatic Diameter Control (ADC) software, commercially available from, for example, FEC Crystal Growing Systems, which can control the shape of the growing crystal, temperature increase, cooling rates, and other pertinent parameters. Crystal growth

15   is commenced by heating a growth chamber of a suitable crucible, such as an iridium crucible, containing thoroughly mixed powders of magnesium oxide (MgO), cobalt oxide (Co_3O_4) and aluminum oxide (Al_2O_3). The growth chamber is heated to a suitable temperature, such as a temperature in a range of between about 1900°C and about 2150°C. Preferably, the growth chamber is heated to a temperature of about

20   2150°C to form a melt.

The spinel seed is immersed into the molten mixture and rotated while being withdrawn from the growth medium at a controlled rate. In one embodiment, the withdrawal rate is in a range of between about 0.25 and about 1.0 millimeters per hour at a rotation speed in a range of between about 4 and about 12 revolutions per

25   minute (RPM). Preferably, the withdrawal rate is about 1 millimeter per hour and the rotation of the seed is about 8 RPMs. Crystal growth continues for a suitable period of time to form a monocrystalline lattice of suitable dimension. In one embodiment, crystal growth is continued for a period of about 150 hours. Thereafter, the crystal is cooled to about 25°C over a period of time in a range of

30   between about 72 and about 100 hours. Preferably, the crystal is cooled from the melt temperature, of about 2150°C to about 25°C over a period of time of about 100

hours. Thereafter, the crystal can be machined by known methods to form the
saturable absorber Q-switch of the invention.

The invention is illustrated by the following examples, which are not
intended to be limiting in any way.

5   EXEMPLIFICATION

EXAMPLE 1 - General Method for Spinel Growth

The various cobalt doped spinel compositions were grown on 1:1 ($MgAl_2O_4$)
spinel seed oriented along the <111> axis. Desired compositions were melted in
iridium crucibles of sizes appropriate for growth of 30 mm diameter, and 50 mm
10   diameter crystals. The sizes of the melts for larger crystals were circa 3000 gms.
The iridium crucibles were inductively heated by 10kHz RF (radio-frequency)
generators. The diameter control was based on controlling the growing crystals
weight via controlling the generator output in accordance to the signal from a load
cell. On an average, the melting point of the spinel was about 100 degrees higher
15   than the melting point of sapphire. Prior to and during the growth, the melts were
maintained under an ambient atmosphere strictly inert. The volatility of the Co
oxide dopant was very low. The Co oxide apparently reacted with the spinel
components on the heat up, and did not evaporate from the melt. The crystals of 1:1
and 1:2 compositions appeared to grow relatively easily, with linear growth rates
20   exceeding 1-2 mm/hr. The charge preparation in a case of the 1:3 compound
included a very thorough mixing of the constituent oxides. In addition, the results
were sensitive to establishing a good equilibrium condition during seeding of the
crystal, and also to the crystal growth rate.

EXAMPLE 1A - 1:3 Spinel Growth

Composition:

206.05 gms of MgO

0.41 gms of Co_3O_4

5   1043.54 gms of Al_2O_3

The composition was mixed and loaded into 3" diameter 4-1/2" tall iridium crucible

of 440 ml volume. The crucible was placed into growth system comprising RF

(radio frequency), generator (power) supply, a growth chamber containing the RF

coupling coil, zirconium oxide insulation material in an ambient gas enclosure -

10   "Bell Jar," and an electronic control system. Control was accomplished by

controlling the RF generator output in response to the mass of the growing crystal.

"ADC" (Automatic Diameter Control) software, supplied by F. Bruni, controlled the

shape of growing crystal, temperature increase, and cool down rates, and all other

pertinent parameters. The crucible with the oxide mixture was heated to 2150°C to

15   form a melt. <111> spinel "seed" (small rod-shaped crystal) was immersed (dipped)

into the molten mixture. Applying a withdrawal rate of 1 mm/hr along with rotation

of the seed at 8 rpm, the crystal growth was started. Growth continued for 150 hours

followed by a 100 hour cool down period.

Result: A blue crystal, "Spinel" crystal structure, 1/4" diameter, 7" long A_0 =

20    $8.012A^0$

Optical measurement: O.D. (Optical Density): $0.7\ cm^{-1}$

EXAMPLE 1B - 1:2 Spinel Growth

Composition:

  141.56 gms of MgO

   0.87 gms of Co_3O_4

5   1107 gms of Al_2O_3

The composition was loaded into same crucible as described in Example #1, and
placed in an identical growth system. Heat-up time was 6 hours to 2150°C.
Rotation rate applied was 8 rpm, pull rate 1 mm/hr under strictly inert atmosphere.
Growth time of 150 hours was followed by a 100 hour cool-down period. Grown
10 crystal was harvested at room temperature.

Result: A blue crystal

  Structure: "Spinel"

   $A_0 = 7.97$ A^0

  Optical Density: 2.4 cm^{-1}

15 EXAMPLE 1C - 1:1 Spinel Growth

Composition:

  353.68 gms of MgO

   0.70 gms of CO_2O_3

  895.62 gms of Al_2O_3

20 Raw materials were mixed and loaded into an iridium crucible. The crucible was
placed in the previously described system. Temperature was increased over a period
of 6 hours to 2150°C to complete melting. <111> spinel seed was immersed
(dipped) into the melt. A withdrawal rate of 1 mm/hr, crystal growth was started.
Growth continued for 150 hours followed by a 100 hour cool down period.

Result: A single crystal spinel 1/4" diameter, 7" long

Structure: "Spinel"

Optical Density: 0.63 cm^{-1}

EXAMPLE 2

5   Experimental Details

Crystals of $MgAl_2O_4$, $MgAl_4O_7$, and $MgAl_6O_{10}$ doped with varying amounts

of cobalt from 0.02 to 0.04 percent atomic cobalt were grown by the method

described in Example 1. We labeled the different spinels according to 1:1

($MgO \cdot Al_2O_3$), 1:2 ($MgO \cdot 2Al_2O_3$), and 1:3 ($MgO \cdot 3Al_2O_3$). The structural analysis for

10   each crystal gave unit cell dimensions of 8.083 Å for 1:1, 8.012 Å for 1:2, and 7.970

Å for 1:3. Each spinel belonged to the space group O_h^7-Fd3m with the Mg^{2+} ions

having tetrahedral coordination with full T_d symmetry and the Al^{3+} ions having

octahedral coordination (P. R. Staszak, et al., J. Phys C: Solid State Phys., 17:4751

(1984) and H. St. C. O'Neill and A. Navrotsky, Am. Mineralogist, 68:181 (1983),

15   the teachings of which are incorporated herein by reference in their entirety). The

lattice constant for 1:1 reported in the literature was 8.085 Å (R. D. Gillen and R. E.

Salomon, J. Phys. Chem., 74:4252 (1970), the teachings of which are incorporated

herein by reference in their entirety). Previous studies, including thermodynamic

phase diagram analyses of $MgO \cdot nAl_2O_3$ and optical studies of Co^{2+}, showed a strong

20   preference for Co^{2+} in tetrahedral sites when the crystal had both tetrahedral and

octahedral cation sites (A. Navrotsky and O. J. Kleppa, J. Inorg. Nucl. Chem.,

29:2701 (1967); A. Navrotsky and O. J. Kleppa, J. Inorg. Nucl. Chem., 30:479

(1968); A. Navrotsky, et al., J. Am. Ceramic Soc., 69:418 (1986); A. Navrotsky, Am.

Mineralogist, 79:589 (1994); and N. V. Kuleshov, et al., J. Luminescence, 55:265

25   (1993), the teachings of which are incorporated herein by reference in their entirety).

Our results, described infra, indicated that the tetrahedral site were preferred sites of

occupation by Co^{2+}.

Polished samples used in spectroscopic measurements ranged from circular

disks 4 cm in diameter and 0.5 cm thick, to rectangular pieces for low-temperature

studies that measured 10mm by 5mm by 2.15mm thick. Crystals having the optimum optical density at 1.54 μm were examined for use as saturable absorbers. Room temperature absorption spectra were obtained between 3000nm and 300nm with a Perkin-Elmer Lambda-nine spectrophotometer. Calibration of the instrument

5   over the wavelength of interest indicated that spectral lines and bands were measured to an accuracy of 0.22nm. The low temperature (8K) absorption spectrum was obtained with an upgraded Cary Model 14R spectrophotometer controlled by a desktop computer. The spectral bandwidth was set at 0.5nm and the instrument was internally calibrated to an accuracy of 0.3nm. Spectra were analyzed and plotted by

10   using the computer software program Sigma Plot. Fluorescence spectra at room temperature and at 8K were also obtained by using the instrument together with appropriate mirrors and filters and a Spex Model 340 E monochromator. For fluorescence studies, excitation at 514.5nm was provided by an argon ion laser.

For low-temperature studies, the sample was mounted at the cold finger of a

15   CTI Model-22 closed-cycle helium cryogenic refrigerator capable of operation between 8K and room temperature. The sample temperature was monitored with a silicon-diode sensor attached to the base of the sample holder and maintained by using a Lake Shore control unit.

The fluorescence lifetime of the strongest emission band centered between

20   650nm and 700nm was measured by exciting each sample with the second harmonic (532nm) of a Quanta-Ray pulsed Nd:YAG laser Model GCR-12S. The pulse width was about 6ns and the beam divergence was less than 0.5 μrad. The output energy was 150mJ at 10Hz. The signal was detected by a photomultiplier tube attached to the exit slit of the monochromator and sent to a 150 MHZ Tektronix oscilloscope

25   Model 2445A having a resolution of 10ns.

Observed Spectra

The room temperature absorption spectrum of Co^{2+} in the three spinel crystals is given in Table 1. The concentration of Co^{2+} in each sample was 0.033% (atomic weight percent, or "at.") Co for 1:1, 0.02% at. Co for 1:2, and 0.0429% at.

30   Co for 1:3. The general features in all three spectra were similar and consisted of

two relatively strong bands centered near 600nm and 1350nm and weaker bands

appearing between 550nm and 470nm, and between 2500nm and 1900nm (N. V.

Kuleshov, *et al., J. Luminescence, 55*:265 (1993), the teachings of which are

incorporated herein by reference in their entirety). However, comparable peaks and

5   bands showed a noticeable shift to longer wavelengths from the 1:1 crystals to the

1:3 crystals. Of particular interest was the shift of the $^4T_1$ spectrum of Co^{2+} in the 1:3

sample to wavelengths even more favorable for Q-switching at 1.54 μm than the

saturable absorber Co^{2+}:$MgAl_2O_4$ (the 1:1 host crystal) (J. B. Gruber, *et al., Proc. of

SPIE, 3928*:142 (2000), the teachings of which are incorporated herein by reference

10   in their entirety). The peak at 1544nm was observed where stimulated emission

occurred in the Er:Yb:glass laser. Its estimated absorption cross section at this

wavelength was higher than the value employed for Co^{2+}:$MgAl_2O_4$ ($4 \times 10^{-19} cm^2$) and

was considerably larger than the stimulated emission cross section of Qx/Er at

1535nm ($0.6 \times 10^{-20} cm^2$) (V. P. Mikhailov, *et al., OSA TOPS, 21(ASSL)*:145 (1999);

15   M. B. Carmargo, *et al., Opt. Letts, 20*:339 (1995); J. B. Gruber, *et al., Proc. of SPIE,

3928*:142 (2000); and R. Wu, *et al., OSA TOPS, 22(ASSL)*:421 (2000), the teachings

of which are incorporated herein by reference in their entirety). Excited state

absorption (ESA) for Co^{2+} near 1540nm in 1:1 samples has been reported by several

groups (V. P. Mikhailov, *et al., OSA TOPS, 21(ASSL)*:145 (1999); M. B. Carmargo,

20   *et al., Opt. Letts, 20*:339 (1995); and M. Birnbaum, *et al. OSA TOPS, 19(ASSL)*:148

(1997)) including our group (J. B. Gruber, *et al., Proc. of SPIE, 3928*:142 (2000))

that has done extensive modeling studies on saturable absorbers. The ESA cross

section for Co^{2+} in the 1:3 compound, was similar to the value reported by Co^{2+} in

the 1:1 compound (M. B. Carmargo, *et al., Opt. Letts, 20*:339 (1995)).

25   The similarity in the room temperature spectra of the three samples led us to

examine the details of the absorption spectrum for Co^{2+}:$MgAl_4O_{10}$ at 8K. Table II

presents the absorption spectrum between 2590nm and 476.5nm. Figs. 2 and 3 show

light absorption of the 1:3 spinel as a function of wavelength at 8 Kelvin and 300

Kelvin, respectively. The pattern of light absorption between 1200 mm and 1600

30   mm indicates possible use of this material for passive Q-switches for "eye-safe"

(1.546μ (micron)) lasers, but also for lasers operating in a range of between about

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1.3 and about 1.35µ, which is useful in medicine as well as in optical

communications business. The comparison at the two temperatures indicates that

the material also is useful at room temperature. The observed spectra were similar

to the spectra reported earlier for Co^{2+} ions in tetrahedral sites in $MgAl_2O_4$ (N. V.

5   Kuleshov, et al., J. Luminescence, 55:265 (1993), the teachings of which are

incorporated herein by reference in their entirety). There were some differences in

the magnitude of the crystal-field splitting of Co^{2+} in tetrahedral sites which can be

seen by comparing the energy levels in Table II., col. 5, with the energy levels of

Co^{2+} in $ZnAl_2O_4$, for which the data of Ferguson, et al. (J. Ferguson, et al., J. Chem.

10   Phys., 51:2904 (1969)) allowed us to do extensive modeling (J. B. Gruber, et al.,

Proc. of SPIE, 3928:142 (2000). Table II, Col. 2, shows the Tanabe-Sugano labels

where (^{2S+1}L) represents the principal state (either quartet or doublet); the

wavelength, absorption coefficient and the energy of the transition are given in Cols.

3-5. The energy-level calculations and modeling are described below.

15   The fluorescence spectra at 8K and at 300K were characterized by a strong

emission band between 600nm and 700nm. As can be seen in Figures 4, 5 and 6,

fluorescence emissions as a function of wavelength of 1:3 spinels are comparable at

8 Kelvin and 300 Kelvin. These materials are useful as active materials for broadly

tunable lasers. Also, two very weak, broad bands centered around 920nm and

20   1300nm which typically were observed only in more concentrated samples (N. V.

Kuleshov, et al., J. Luminescence, 55:265 (1993)). The assignment of the transitions

could be made with help from the analysis of the levels given in Table II. The strong

red emission band centered at 660nm was due to vibronic and electronic transitions

from the ^2E, $^4T_1$ excited states to the ground state, $^4A_2$, the weak broad band observed

25   at 920nm represented similar transition types from ^2E, $^4T_1$ to the $^4T_2$ state, and the

weak band around 1300nm represented vibronic and electronic transitions from ^2E,

$^4T_1$ to the $^4T_1$ manifold observed in absorption between 1540nm to 1230nm. A weak

band observed at 725nm at 8K may have represented $^2A_1\square^4T_2$ transitions (see Fig.

5).

30   The room temperature fluorescence of the $Co^{2+}(^2E^4T_1)$ state was a single

exponential, and the lifetime was measured to be about 30 µs. The emission

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intensity did not appear to change appreciably with decrease in temperature to 8K, and so we did not expect the low temperature lifetime to vary significantly from the room temperature value. Using crystals of the 1:1 sample containing between ten and twenty times more Co^{2+} than we report, in Table II, for $Co^{2+}:MgAl_4O_{10}$.

5   Kuleshov, *et al.* (N. V. Kuleshov, *et al., J. Luminescence,* 55:265 (1993)), found that the luminescence lifetime for all three bands was the same. The emission decay was strongly nonexponential and dependent on the temperature and Co^{2+} ion concentration. However, their results were expected given the extent to which the $3d^7$ orbitals interacted with the lattice of the host crystal at such Co^{2+} ion

10   concentrations.

Energy Levels of Co^{2+}

       The absorption spectra of Co^{2+} ($3d^7$) in tetrahedral cation sites of the spinels consist of vibronically-coupled electronic transitions (including zero-phonon transitions) from the ground state $^4A_2(^4F)$ to excited quartet states such as $^4T_2(^4F)$ and

15    $^4T_1(^4P)$, and excited doublet states, including $^2E(^2G)$, $^2T_1(^2G)$, $^2A_1(^2G)$, $^2T_1(^2P)$, and $^2T_2(^2H)$. The electronic (Stark) levels for the $3d^7$ configuration are determined using a Hamiltonian that consists of atomic and crystal-field terms (C. A. Morrison, "Crystal Fields for Transition-Metal Ions in Laser Host Materials," (Springer, New York) (1992), the teachings of which are incorporated herein by reference in their

20   entirety). The atomic or "free-ion" part is given as,

$$\hat{H}_{FI} = \sum_{k=2,4} F^{(K)} \sum_{i>j} C''_{kq}(i) \, C_{kq}(j) + \alpha \hat{L} \, (\hat{L}+1) + \gamma \, \hat{G} \, (R_5) + \zeta_d \sum_j \bar{l}_j \cdot \bar{s}_l \, , \qquad (1)$$

where $F^{(k)}$ are the Slater coulombic repulsion parameters between equivalent d

25   electrons, α and γ are interconfiguration parameters and ζ_d is the spin-orbit coupling parameter for the 3d electrons (C. A. Morrison, "Angular Momentum Theory Applied to Interactions in Solids," (Springer, New York) (1988), the teachings of which are incorporated herein by reference in their entirety). The crystal-field terms for Co^{2+} in tetrahedral sites are given as,

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$$\hat{H}_{CF} = B_{20} \sum_i C_{20}(i) + B_{40} \sum_i C_{20}(i) + B_{44} \sum_i [C_{44}(i) + C_{4-4}(i)], \qquad (2)$$

where the B_{nm} represent crystal-field parameters that are related to the lattice-sum parameters, A_{nm}, through the three-parameter theory with $B_{nm} = \rho_n A_{nm}$ (C. A.

5   Morrison, *et al., Chem. Phys.,* 154:437 (1991), the teachings of which are incorporated herein by reference in their entirety). The initial set of atomic and crystal-field parameters are listed in Table III and are obtained from several sources (C. A. Morrison, "Crystal Fields for Transition-Metal Ions in Laser Host Materials," (Springer, New York) (1992). We treat $F^{(k)}$ and the three B_{nm} parameters as

10   adjustable, beginning with a set of $F^{(2)}$ and $F^{(4)}$ proposed originally by Morrison (C. A. Morrison, "Crystal Fields for Transition-Metal Ions in Laser Host Materials," (Springer, New York) (1992)) and an initial set of B_{nm} based on lattice-sum modeling using ion separations based on our x-ray crystallography studies of the spinel series.

15   Matrix elements for the Hamiltonian were computed using coefficients of fractional parentage for the $3d^7$ electronic configuration. The complete Hamiltonian was diagonalized in the basis states S,L, and the calculated levels for Co^{2+} in $MgAl_6O_{10}$ are given as an example in Table II, Col. 6. The splitting of the ground-state, $^4A_2(^4F)$ was not fully resolved in the temperature-dependent spectra. The

20   predicted splitting given in table II is 5cm^{-1}. The observed splitting in Co^{2+}:$ZnAl_2O_4$, wherein Co^{2+} occupies the Zn^{2+} tetrahedral site, was 12 cm^{-1} (J. Ferguson, *et al., J. Chem. Phys.,* 51:2904 (1969), the teachings of which are incorporated herein by reference in their entirety). Only one of the observed levels was used to establish the energy of the $^4T_2(^4F)$ state since the spectra of this manifold were very weak in the

25   0.0429% at Co spectrum reported in Table II. Longer pathlengths and greater concentrations of Co^{2+} provided spectra that support the predicted levels 3 through 8 for this manifold splitting. Levels 15 through 25 showed a strong mixing of ^2G states into the ^4P states (Col. 7, Table II). Many of the zero-phonon transitions allowed in T_d symmetry were obscured by the vibronic bands making it difficult to

30   attempt an overall fitting of the observed-to-calculated energy levels. However, the

continuity in general band shape and structure throughout the series was predicted very well, with the final set of spectroscopic parameters given in Table III.

Table I. Room temperature absorption bands of Co^{2+} in $MgO \cdot nAl_2O_3$

STATEᵃ	MgAl₂O₄			MgAl₄O₇			MgAl₆O₁₀		
	$\lambda(nm)^b$	$\alpha^c(cm^{-1})$	$E(cm^{-1})^d$	$\lambda(nm)^b$	$\alpha(cm^{-1})^c$	$E(cm^{-1})^d$	$\lambda(nm)^b$	$\alpha(cm^{-1})^c$	$E(cm^{-1})^d$
$^4T_2$	2519	0.03	3970	2556	0.04	3912	2580	0.05	3870
	2448	0.03	4085	2476	0.04	4039	2500	0.04	4000
(^4F)				2365(sh)	0.05	4228	2390(sh)	0.05	4184
	2252	0.05	4441	2279	0.07	4388	2300	0.09	4347
	2163	0.03	4623	2190(sh)	0.05	4566	2220(sh)	0.06	4505
$^4T_1$	1536	5.21	6510	1537	5.78	6506	1544	5.91	6476
(^4F)	1417	4.82	7057	1450	5.12	6897	1460(sh)	5.32	6849
	1350	5.03	7407	1360	5.32	7353	1365	5.50	7326
	1229	4.36	8137	1234	4.72	8104	1238	4.50	8077
$^2E(^2G)$	671	1.36	14900	672	1.28	14880	675	1.31	14815
$^4T_1$	625	16.3	16000	626	14.3	15974	628	15.6	15923
(^4P)	598	15.9	16722	599	14.7	16694	598	15.2	16700
	580	17.1	17241	581	16.0	17211	583	17.2	17150
$^2A_1$ (^2G)	545	2.8	18343	545	2.8	18348	546	2.6	18315
$^2T_1$ (^2P)	475	0.8	21053	476	0.7	21008	476.5	0.8	20986

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a) Tanabe/Sugano label; principal state is given in parentheses.

b) Wavelength is given in nanometers; sh denotes well-defined shoulder.

c) Absorption coefficient is given in cm^{-1}

d) Energy is given in wavenumbers.

Table II. Absorption spectra of Co^{2+} in $MgAl_4O_{10}$ at 8K[a]

Level	State	$MgAl_4O_{10}$			$E(cm^{-1})$ Calc.[b]	Mixture SL States[c]
		$\lambda(nm)_{abc}$	$\alpha(cm^{-1})$	$E(cm^{-1})$		
1	$^4A_2$			0	-7	$1.00\,^4F$
2	(^4F)				-2	$1.00\,^4F$
3	$^4T_2$	2590	vwk	3861	3728	$0.98\,^4F+0.01\,^4P+0.01\,^1G$
4	(^4F)	2500(b)	vwk	4000	4019	$0.99\,^4F+0.01\,^2G$
5		2400(b)	vwk	4166	4146	$0.99\,^4F+0.01\,^4P$
6					4411	$0.99\,^4F+0.01\,^4P$
7		2231.5^d	1.11	4481	4544	$0.99\,^4F+0.01\,^4P$
8		2110	vwk	4739	4713	$0.99+\,^4F+0.01\,^4P$
9	$^4T_1$	1539^d	5.33	6498	6479	$0.91\,^4F+0.09\,^4P$
10	(^4F)	1460(sh)	4.82	6849	6854	$0.86\,^4F+0.13\,^4P+0.01\,^2G$
11		1337^d	5.24	7479	7507	$0.99\,^4F+0.01\,^4P$
12					7925	$0.95\,^4F+0.01\,^4P+0.01\,^2D(2)$
13		1241^d	4.17	8058	8065	$0.91\,^4F+0.08\,^4P+0.01\,^2D(2)$
14		1230(sh)	3.82	8130	8119	$0.97\,^4F+0.02\,^4P+0.01\,^2D(2)$
15	^2E	673^d	1.12	14860	14877	$0.39\,^2G+0.20\,^4P+0.15\,^2P$
16	(^2G)	670(sh)	1.00	14925	14913	$0.56\,^2G+0.17\,^4P+0.15\,^4F$
17	$^4T_1$	Band	3.0	15267	15246	$0.65\,^4P+0.18\,^2G+0.11\,^4F$

18	(^{4}P)	Band		un-resolved band	15356	$0.45\,^2G+0.18\,^2P+0.15\,^4P$
19		Band			15357	$0.66\,^2G+0.13\,^2D(2)+0.09\,^2H$
20		Band			15690	$0.49\,^2G+0.20\,^2P+0.16\,^2H$
21					15718	$0.48\,^4P+0.24\,^2G+0.14\,^2P$
22		621^d	15.07	16103	16167	$0.90\,^4P+0.06\,^2G+0.02\,^4F$
23		605^d	16.1	16529	16451	$0.67\,^4P+0.22\,^2G+0.04\,^2H$
24		598	17.40	16722	16696	$0.82\,^4P+0.11\,^2G+0.02\,^2H$
25		583(b)	18.1	17150	16852	$0.70\,^4P+0.23\,^2G+0.04\,^2H$
26	$^2A_1$	552(sh)	11.0	18116	18080	$0.65\,^2G+0.21\,^4P+0.07\,^2D(1)$
27	(^{2}G)	546^d	9.3	18315	18286	$0.85\,^2G+0.09\,^2D(2)+0.03\,^2D(1)$
28					18389	$0.87\,^2G+0.05\,^2D(2)+0.07\,^2H$
29		Band			18746	$0.63\,^2G+0.24\,^2D(2)+0.08\,^2D(1)$
30					19831	$0.42\,^2G+0.37\,^2P+0.12\,^2H$
31		500^d	0.7	20000	19870	$0.43\,^2G+0.40\,^2P+0.09\,^2H$
32	$^2T_1$	490(sh)	0.50	20408	20494	$0.62\,^2P+0.23\,^2G+0.08\,^2H$
33	(^{2}P)	476.5^d	0.60	20986	20862	$0.34\,^2H+0.25\,^2G+0.23\,^2D(2)$
34	$^2T_2$				21476	$0.45\,^2H+0.24\,^2D(2)+0.18\,^2G$
35	(^{2}H)				21906	$0.41\,^2D(2)+0.36\,^2H+0.10\,^2D(1)$

a) Sample contained 0.0429% at. Co.

b) Parameters: $F^2 = 61542$, $F^4 = 40168$, $\alpha = 108$, $\zeta_d = 515$, $B_{20} = 3949$, $B_{40} = -9081$, $B_{44} = 5242$ (Co^{2+} in tetrahedral sites).

c) Mixture of ^{2S+1}L states in the wave function of the energy level.

d) Levels used in calculations.

Table III. Spectroscopic parameters for Co^{2+} in T_d sites[a]

Parameter	MgAl₂O₄ Initial value (cm⁻¹)[b]	Final Value (cm⁻¹)	MgAl₄O₇ Initial Value (cm⁻¹)[c]	Final Value (cm⁻¹)	MgAl₆O₁₀ Initial Value (cm⁻¹)[d]	Final Value (cm⁻¹)
$F^{(2)}$	59367	59746	60520	61050	61045	61542
$F^{(4)}$	42210	41946	41843	41325	41705	40168
B_{20}	2720	2566	2641	2814	3119	3949
B_{40}	-8640	-8693	-8714	-8920	-9267	-9081
B_{44}	5163	5120	5092	5040	5171	5242
ζ_d	420	420	537	537	515	515
α	86	86	108	108	108	108

a) Only $F^{(2)}$, $F^{(4)}$, and B_{nm} parameters varied, within each spinel

b) C. A. Morrison, "Crystal Fields for Transition-Metal Ions in Laser Host Materials"

(Springer, New York) (1992).

c) C. A. Morrison, unpublished (1996).

d) C. A. Morrison, unpublished (1996).

Modeling of Crystals as Saturable Absorbers

Co²⁺ has been modeled as a saturable absorber for passively Q-switching the eyesafe (1.54μm) Er:Yb:glass laser (J. B. Gruber, et al., Proc. of SPIE, 3928:142 (2000)). The model makes use of the rate equations based on quasi-three level gain medium and a four-level absorber that includes excited-state absorption (ESA). The model was expanded to include energy transfer between Yb and Er and excited state absorption in the gain medium. The spectroscopic parameters for the various gain media are available in the open literature (J. B. Gruber, et al., Proc. of SPIE, 3928:142 (2000), the teachings of which are incorporated herein by reference in their entirety)). For the saturable absorber Co²⁺:MgAl₆O₁₀, which we modeled recently, we used concentrations equivalent to that reported in the present study; an index of

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refraction we determined near 1.54μm (1.742); an experimental $\sigma(gs)=5.2\times10^{-19}cm^2$; an experimental $\sigma(es)=1.87\times10^{-19}cm^2$, and a delay time ($\tau_{31}$) of 30×10^{-6}s.

The 1:3 material is a better performer as a saturable absorber than 1:1 and 1:2 spinels given comparable Co^{2+} ion concentrations and a laser cavity design that

5   is the same for all three spinel samples.

In summary, all members of the series may prove to be efficient high performance absorbers for Q-switching at the 1:54 μm wavelength.

EQUIVALENTS

While this invention has been particularly shown and described with

10   references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

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CLAIMS

What is claimed is:

1. A saturable absorber Q-switch, comprising a monocrystalline lattice having a formula $Mg_{1-x}Co_xAl_yO_z$ where x is greater than 0 and less than about 1, y is greater than 2 and less than about 8, and z is between about 4 and about 13, said lattice having tetrahedral and octahedral positions, and wherein most of the magnesium and cobalt occupy tetrahedral positions.

2. The saturable absorber Q-switch of Claim 1, wherein essentially all of the cobalt and magnesium occupy tetrahedral positions.

3. The saturable absorber Q-switch of Claim 2, wherein the unit cell dimension is between about 7.970Å and about 8.083 Å.

4. The saturable absorber Q-switch of Claim 3, wherein z is about 4.

5. The saturable absorber Q-switch of Claim 3, wherein y is about 4 and z is about 7.

6. The saturable absorber Q-switch of Claim 3, wherein y is about 6 and z is about 10.

7. The saturable absorber Q-switch of Claim 3, wherein cobalt is present in the monocrystalline lattice in an amount between about 0.02 atomic weight percent and about 0.043 atomic weight percent.

8. The saturable absorber Q-switch of Claim 1, having an absorption band of between about 1537 and about 1544nm.

9.   The saturable absorber Q-switch of Claim 8, having an absorption band of about 1537nm.

10.   The saturable absorber Q-switch of Claim 8, having an absorption band of about 1539nm.

5   11.   The saturable absorber Q-switch of Claim 8, having an absorption band of about 1544nm.

12.   The saturable absorber Q-switch of Claim 1, having an absorption band of about 1337nm.

13.   The saturable absorber Q-switch of Claim 1, having an absorption band of
10   about 1360nm.

14.   The saturable absorber Q-switch of Claim 1, having an absorption band of about 1365nm.

15.   The saturable absorber Q-switch of Claim 1, having a decay time, τ_{31}, greater than about 30×10^{-6} seconds.

15   16.   A laser system, comprising:
      a)   a laser resonator cavity defined by a flat mirror and an outcoupler mirror, said flat mirror and said outcoupler mirror oriented to form an optical resonant axis;
      b)   a lasing element within the laser resonator cavity;
20   c)   optical pumping means proximate to said lasing element; and
      d)   a saturable absorber Q-switch lying along the resonant axis, said Q-switch including a monocrystalline lattice having a formula $Mg_{1-x}Co_xAl_yO_z$, where x is greater than 0 and less than about 1, y is greater than 2 and less than about 8, and z is between about 4 and

about 13, said lattice having tetrahedral and octahedral positions, and wherein most of the magnesium and cobalt occupy tetrahedral positions.

17. The laser system of Claim 16, wherein essentially all of the magnesium and cobalt occupy tetrahedral positions.

18. The laser system of Claim 17, wherein the saturable absorber Q-switch has an absorption band within about 4nm of the lasing transition of the lasing element.

19. The laser system of Claim 18, wherein the saturable absorber Q-switch has an absorption band within about 2nm of the lasing transition of the lasing element.

20. The laser system of Claim 17, wherein the lasing element is an Er:Yb:glass (Er^{3+}:glass?) lasing element.

21. The laser system of Claim 20, wherein the saturable absorber Q-switch has an absorption band of about 1537nm.

22. The laser system of Claim 20, wherein the saturable absorber Q-switch has an absorption band of about 1544nm.

23. The laser system of Claim 17, wherein the lasing element is a Nd^{3+}:$YAlO_3$ lasing element.

24. The laser system of Claim 23, wherein the saturable absorber Q-switch has an absorption band of about 1360nm.

25.　　The laser system of Claim 23, wherein the saturable absorber Q-switch has an absorption band of about 1365nm.

26.　　The laser system of Claim 23, wherein the saturable absorber Q-switch has an absorption band of about 1337nm.

5　27.　　The laser system of Claim 17, wherein the unit cell dimension of the saturable absorber Q-switch is between about 7.970Å and about 8.083Å.

28.　　The laser system of Claim 27, wherein y is about 2 and z is about 4.

29.　　The laser system of Claim 23, wherein y is about 4 and z is about 7.

30.　　The laser system of Claim 27, wherein y is about 6 and z is about 10.

10　31.　　The laser system of Claim 27, wherein cobalt is present in the monocrystalline lattice in an amount between about 0.020 atomic weight percent and about 0.043 atomic weight percent.

32.　　The laser system of Claim 17, wherein saturable absorber Q-switch has a decay time, τ_{31}, greater than about 30×10^{-6} seconds.

15　33.　　A method of forming a monocrystalline lattice of a saturable absorber Q-switch, comprising the steps of:

　　　　a)　　forming a melt that includes magnesium, cobalt, aluminum and oxygen, wherein the molar ratio of magnesium:cobalt:aluminum is (1-x):x:y, where x is greater than 0 and less than about 1, and y is

20　　　　　　greater than 2 and less than about 8;

　　　　b)　　immersing a spinel seed crystal in the melt; and

　　　　c)　　rotating the seed crystal at a rate in a range of between about 2 and about 12 revolutions per minute, while withdrawing the seed crystal

from the melt at a rate in a range of between about 0.04"/hr and about 0.1"/hr to thereby form said monocrystalline lattice.

34. The method of Claim 33, wherein the melt is formed by a method, comprising the steps of:

    a)   combining MgO, Co_3O_4 and Al_2O_3 powders; and

    b)   heating the combined powders to a temperature sufficient to form the melt.

35. The method of Claim 34, wherein the spinel seed crystal is cylindrical.

36. The method of Claim 35, wherein the spinel seed is aligned along a <111> axis in the melt.

37. The method of Claim 36, wherein growth of the crystal continues for a period of time in a range of between about 200 and about 800 hours to form a crystal having a weight in a range of between about 200 and about 2500 gms.

38. The method of Claim 37, wherein the crystal has a diameter in a range of between about 1.25" and about 3".

39. The method of Claim 38, wherein the melt is heated to a temperature greater than about 2150°C.

40. The method of Claim 39, wherein the crystal is cooled to a temperature in a range of between about 20°C and 30°C over a period of time in a range of between about 48 and about 120 hours.

41. The method of Claim 33, wherein y is about 2.

42. The method of Claim 33, wherein y is about 4.

43.   The method of Claim 33, wherein y is about 6.

44.   The method of Claim 33, wherein y is about 8.

45.   The method of Claim 33, wherein x is in a range of between about 0.0001 and about 0.03.

5   46.   The method of Claim 45, wherein cobalt is present in the melt in a range of between about 0.020 atomic weight percent and about 0.043 atomic weight percent.

47.   In a saturable absorber Q-switch that includes a monocrystalline lattice of cobalt-doped spinel:

10   The improvement comprising a molar ratio of aluminum to the combined molar amount of cobalt and magnesium that is greater than 2, and wherein essentially all of the cobalt and magnesium occupy tetrahedral positions of the monocrystalline lattice.

FIG. I
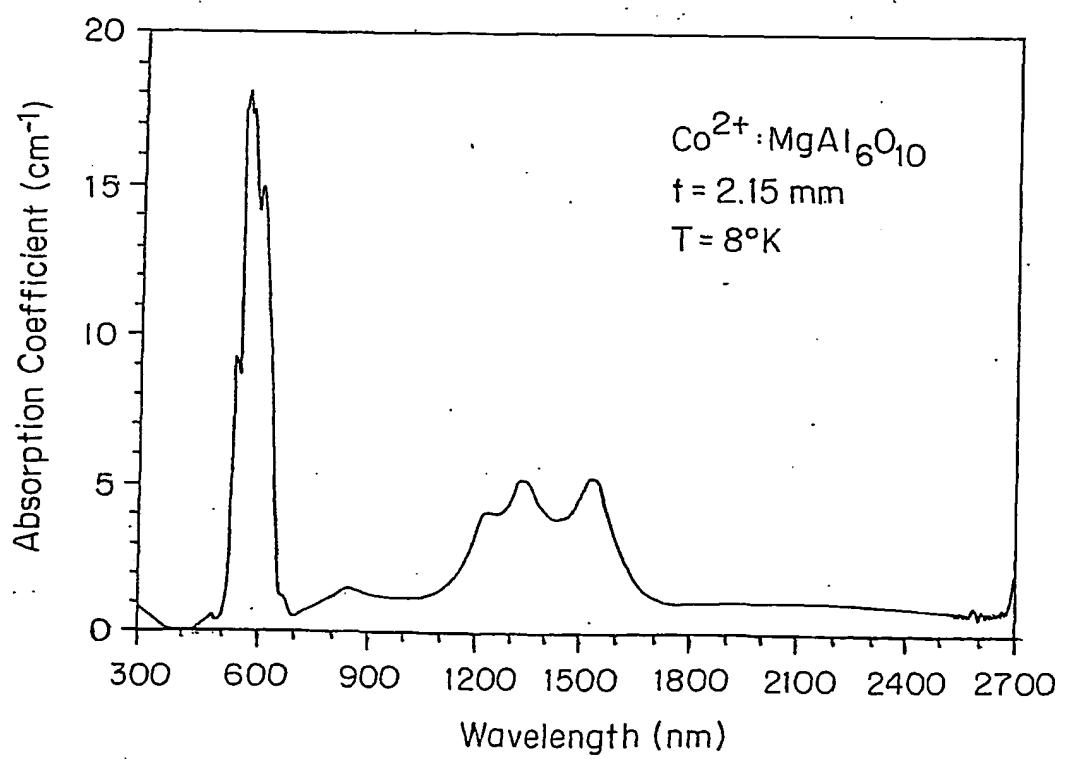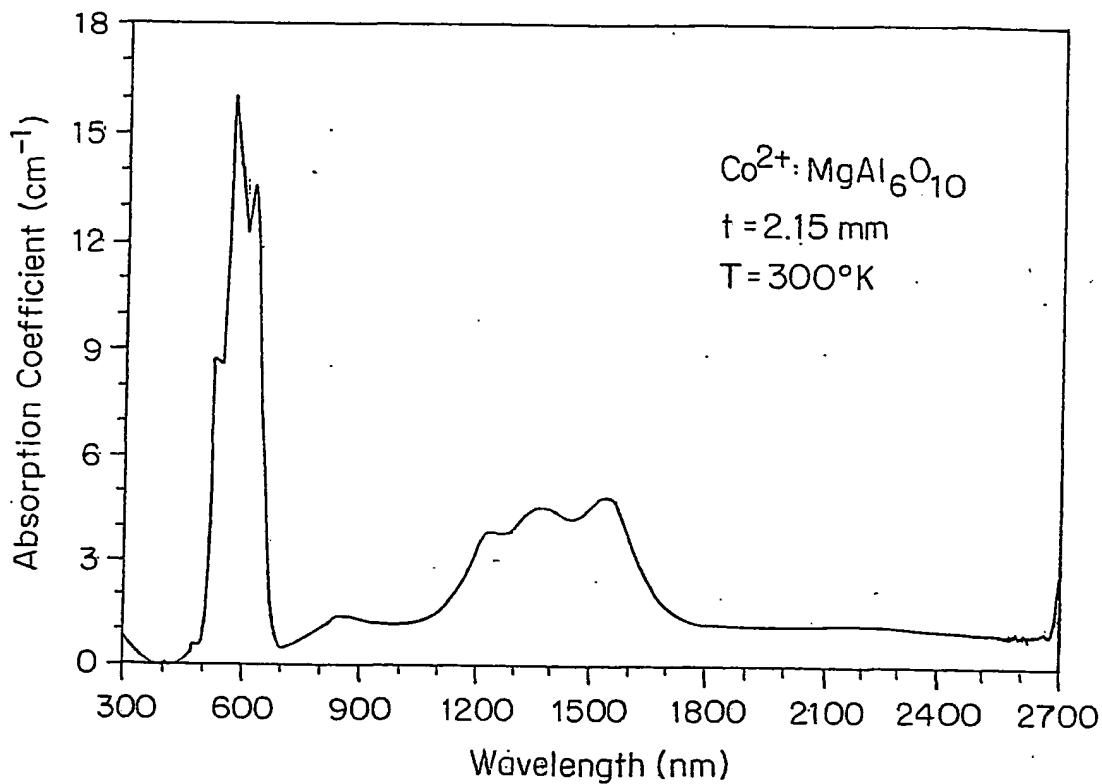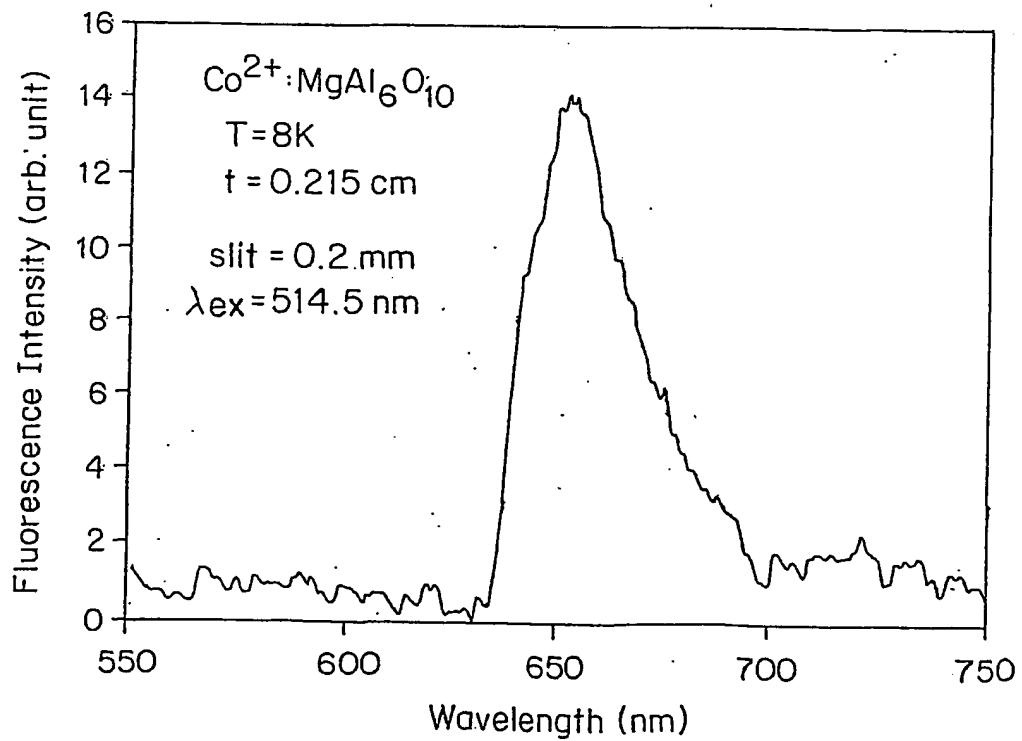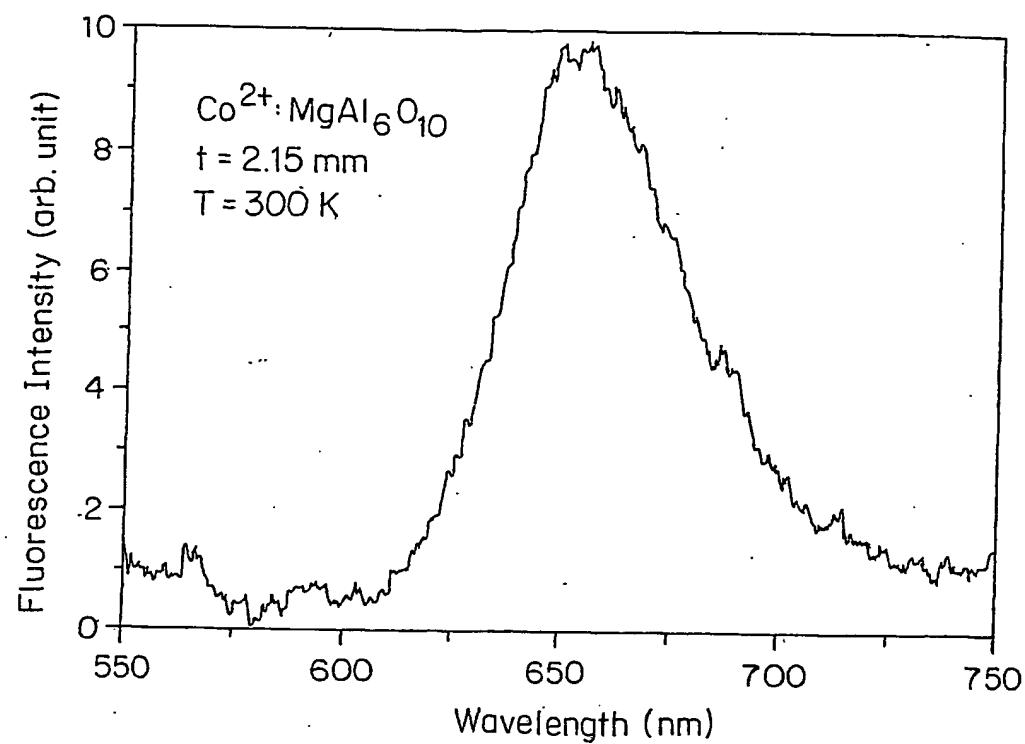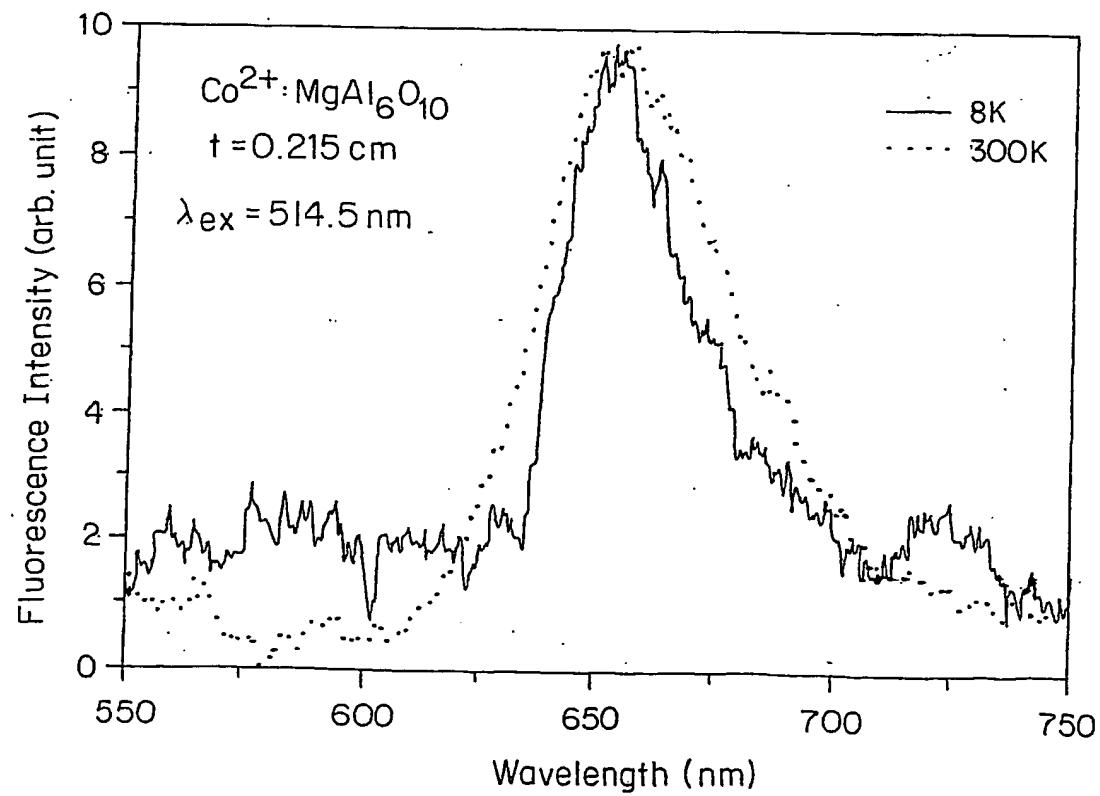
FIG. 2

FIG. 3

Co^{2+}: $MgAl_6O_{10}$

t = 2.15 mm

T = 300°K

FIG. 4

Co^{2+}: $MgAl_6O_{10}$

T = 8K

t = 0.215 cm

slit = 0.2 mm

λex = 514.5 nm

FIG. 5

FIG. 6

GROWTH OF SINGLE CRYSTAL $MgGa_2O_4$ SPINEL

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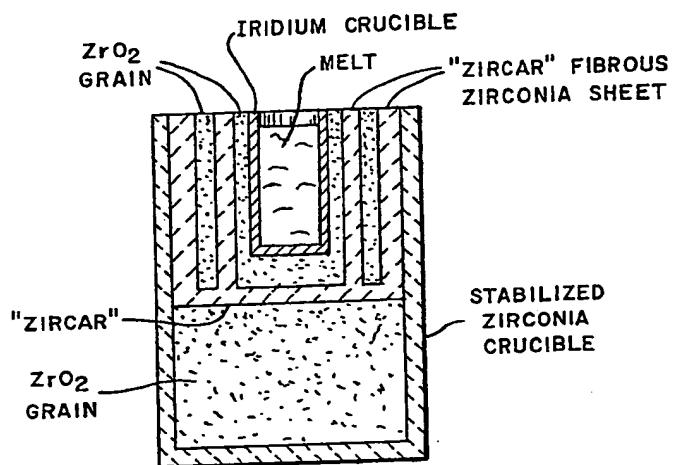
Single-crystal cubic spinel, $MgAl_2O_4$, because of its good insulating and thermal properties, has found important applications in the semiconductor industry, most notably as a substrate for the heteroepitaxial growth of silicon. In addition, some success with the vapor phase epitaxial growth of GaAs on $MgAl_2O_4$ spinel has been reported. The method described below is a technique for the growth of large single crystals of the isostructural material $MgGa_2O_4$, which may serve as a substrate for the heteroepitaxial growth of semiconductors and bubble domain materials. The lattice constant of $MgGa_2O_4$ is $a_o = 8.28$Å compared to $a_o = 8.08$Å for $MgAl_2O_4$. For this reason, $MgGa_2O_4$ would provide a close substrate lattice match for the epitaxial deposition of materials, with the diamond-type structure having larger lattice constants than Si ($a_o = 5.431$Å). Such materials are Ge ($a_o = 5.65$Å), GaAs ($a_o = 5.654$Å), AlAs ($a_o = 5.62$Å), and InP ($a_o = 5,869$Å), among others. Moreover, the larger oxygen-oxygen distance in the close-packed (111) plane of $MgGa_2O_4$, 3.03Å, compared with sapphire (2.74Å) and $MgAl_2O_4$ (2.86Å), makes this crystal potentially useful as a substrate for bubble domain materials of the hexaferrite [(Pb, Ba) $Fe_{12}O_{19}$] and spinel-types.

The spinel phase in the $MgO-Ga_2O_3$ system exists over the composition range $MgO:Ga_2O_3 = 0.68$ to 1.05 at 1500°C. The maximum melting (congruent) point in this system is believed to occur with $MgO:Ga_2O_3 = 1$ (i.e., $MgGa_2O_4$) at a temperature of about 2000°C. To date only small single crystals of $MgGa_2O_4$ have been obtained using the flux growth technique.